Effective potential in glass forming liquids

Antonio de Candia
Dipartimento di Scienze Fisiche, Università di Napoli, ‘Federico II’
INFM, Unità di Napoli, Italy
Complesso Universitario di Monte Sant’Angelo, Via Cintia, I-80126 Napoli, Italy
E-mail: decandia@na.infn.it

Received 23 September 2004
Accepted 11 January 2005
Published 1 February 2005

Abstract. The effective potential formalism is applied to glass forming liquids, choosing a coupling potential such that the ‘order parameter’, conjugated to the coupling strength, is the mean square displacement of the particles from their position in the quenched reference configuration. The potential is linear in some interval of its argument, signalling the coexistence of two phases in the system, one with low and one with high mean square displacement. Within this formalism, one can also compute the free energy of metastable states and their complexity.

Keywords: supercooled liquids (theory)
The phase space of glassy systems is believed to break up, below some temperature \( T_c \) called the ‘mode-coupling temperature’, into an extensive number of components, called ‘free energy valleys’ or ‘metastable states’, separated by high free energy barriers. On lowering the temperature, the number of valleys accessible to the system becomes lower and lower, until at some temperature \( T_K \), called the ‘Kauzmann temperature’, it becomes non-extensive. The existence of metastable states in the temperature range \( T_K < T < T_c \) can be evidenced by the study of a system coupled to a quenched configuration \([1]–[5]\).

Consider a system described by the variables \( x \), and characterized by the Hamiltonian \( H(x) \). Now switch on a coupling potential \( \mathcal{H}_\epsilon(x_0, x) = -\epsilon Q(x_0, x) \), where \( x_0 \) is a configuration of the system thermalized at temperature \( T \), and then kept fixed (quenched), and \( Q(x_0, x) \) is a measure of the ‘similarity’ between the configurations \( x_0 \) and \( x \) (overlap).

The free energy per particle \( f(\epsilon) \) of the coupled system should be independent from the configuration \( x_0 \) in the thermodynamic limit (self-averaging). The effective potential is defined as the Legendre transform \( v(q) = \max_\epsilon [f(\epsilon) + \epsilon q] \), and corresponds to the free energy of a system constrained at a fixed overlap \( Q(x_0, x) = Nq \) from the reference configuration \( x_0 \), where \( N \) is the number of particles.

The effective potential \( v(q) \) was computed in mean field \( p \)-spin models \([2,3]\), and in glass forming liquids using the hypernetted chain approximation \([4]\). In both cases it was found that, besides the thermodynamically stable minimum at \( q = 0 \), below temperature \( T_c \), a secondary minimum appears, at high values of the overlap, signalling the presence of metastable states. The free energy difference between the two minima of the potential corresponds to the logarithm of the number of free energy valleys, that is the complexity, that vanishes at the thermodynamic glass transition \( T_K \). Below \( T_K \), the thermodynamic properties of the glass can still be evaluated by studying \( m \) coupled replicas of the system, and analytically continuing the free energy to values \( m < 1 \) \([1,6]–[8]\). A review can be found in \([9]\).

It is important to point out that, in finite dimensional systems with short range interactions, free energy barriers are finite below \( T_c \) due to nucleation effects (that is activated or hopping processes), and diverge only at \( T_K \). For temperatures \( T_K < T < T_c \), the time needed to escape from a free energy valley is large but finite. Moreover, the coexistence of different phases implies that the effective potential has to be a convex function of its argument. This means that \( v(q) \) cannot have a secondary minimum, and the dynamical transition \( T_c \) cannot be sharply defined.

In this paper, I will apply the effective potential formalism to simple liquids, choosing a particularly convenient coupling potential. The potential is such that the ‘order parameter’, conjugated to the coupling strength \( \epsilon \), is the mean square displacement (msd) of the particles from their position in the quenched reference configuration\(^1\). Let us consider a liquid composed of \( N \) monatomic particles of mass \( m \) enclosed in a cubic box of side \( L \), interacting with a potential energy \( U(r) \), where \( r \) is a \( 3N \)-dimensional vector representing the positions of the particles, with periodic boundary conditions. The equilibrium free energy per particle, at temperature \( T \), is given by (setting \( k_B = 1 \))

\[
f_{eq}(T) = -\frac{T}{N} \ln \int_{0 < r_i < L} \frac{d^{3N} r}{N! \lambda^{3N}} e^{-\beta U(r)},
\]

\(^1\) A similar coupling potential was already considered in \([7]\), in order to compute the free energy of metastable states.
where the integral is done over an hypercubic box of volume $V^N$, with $V = L^3$, and $\lambda = \hbar \sqrt{2\pi/mT}$ is the thermal wavelength. Let us now consider a (quenched) configuration $r_0$ thermalized at temperature $T$, and define the coupling potential

$$\mathcal{H}_e(r_0, r) = -T \ln \left( \frac{\epsilon_0}{\epsilon} \right)^{3N/2} \sum_{P,T} e^{-\beta \epsilon |r - P Tr_0|^2} ,$$

where $\epsilon \geq 0$ is the coupling strength, and $\epsilon_0 = \pi T (\rho/\epsilon)^{2/3}$, where $\rho = N/V$ is the density of the liquid. The operator $T$ runs over all the discrete translations of step $L$ in the $3N$-dimensional space, and the operator $P$ runs over all the permutations of the particles. The configuration $P T r_0$ runs therefore over all the configurations ‘thermodynamically identical’ to $r_0$. It may be said that configuration $r_0$ is ‘partially annealed’, because those identical configurations are effectively summed over in the partition function. When $\epsilon \to 0$ the potential $\mathcal{H}_e(r_0, r)$ vanishes, as can be seen by doing the substitution

$$\sum_{P,T} e^{-\beta \epsilon |r - P Tr_0|^2} \xrightarrow{\epsilon \to 0} \frac{N!}{V^N} \int d^{3N} r_0 e^{-\beta \epsilon |r - r_0|^2} .$$

(3)

It can be seen, analogously, that $(\partial \mathcal{H}_e/\partial \epsilon)(r_0, r)$ vanishes as well when $\epsilon \to 0$. On the other hand, when $\epsilon > 0$, the potential favours the configurations that, apart from a permutation of the particles, or a discrete translation of step $L$, are ‘near’ to the configuration $r_0$. We can now evaluate the coupled free energy as

$$f(\epsilon) = -\frac{T}{N} \ln \int_{0 < r_i < L} \frac{d^{3N} r}{N!} \frac{\lambda^{3N}}{3N} e^{-\beta U(r) + \mathcal{H}_e(r_0, r)}$$

$$= -\frac{T}{N} \ln \left( \frac{\epsilon_0}{\epsilon} \right)^{3N/2} \int_{-\infty < r_i < \infty} \frac{d^{3N} r}{\lambda^{3N}} e^{-\beta U(r) - \beta |r - r_0|^2} .$$

(4)

where in the last member $U(r)$ has been extended by periodicity outside the domain $0 < r_i < L$. The free energy $f(\epsilon)$ can be also written as

$$f(\epsilon) = -\frac{T}{N} \ln \left( \frac{\epsilon_0}{\epsilon} \right)^{3N/2} \int_0^\infty \int_0^\infty \int_{-\infty < r_i < \infty} \frac{d^{3N} r}{\lambda^{3N}} e^{-\beta N |v(r^2) + \epsilon r^2|} .$$

(5)

where the effective potential $v(r^2)$ is defined by

$$v(r^2) = -\frac{T}{N} \ln \frac{d^{3N} r}{\lambda^{3N}} \delta \left( r^2 - \frac{1}{N} |r - r_0|^2 \right) e^{-\beta U(r)} .$$

(6)

The derivative of the effective potential with respect to $r^2$ can be expressed as

$$\frac{\partial v(r^2)}{\partial r^2} = \frac{3T}{2 r^2} [\vartheta(r^2) - 1] ,$$

(7)

where $\vartheta(r^2) = \beta \langle (r - r_0) \cdot \nabla U \rangle r^2 / 3N$, and the average $\langle \cdots \rangle_{r^2}$ is done at fixed $r^2$ from the configuration $r_0$, with the Boltzmann weight $e^{-\beta U(r)}$. Since $r_0$ is thermalized at temperature $T$, from equation (6) it can be derived that $\lim_{r^2 \to 0} [v(r^2) + (3T/2) \ln(2\pi r^2 / 3\lambda^2)] = u_{eq}(T)$, where $u_{eq}(T)$ is the mean potential energy per particle. The effective potential can then be computed by integration of $\vartheta(r^2)$,

$$v(r^2) = u_{eq}(T) + \frac{3T}{2} \left[ \ln \left( \frac{3\lambda^2}{2e \pi r^2} \right) + \int_0^{r^2} \vartheta(r^2) \, d \ln r^2 \right] .$$

(8)

doi:10.1088/1742-5468/2005/02/L02001
Effective potential in glass forming liquids

It is reasonable to believe that \( f(\epsilon), v(r^2) \) and \( \vartheta(r^2) \) are self-averaging quantities, that is in the thermodynamic limit they do not depend on the configuration \( r_0 \), but only on the temperature at which \( r_0 \) is thermalized. The potential \( v(r^2) \) can be interpreted as the free energy of a system constrained to be at msd \( r^2 \) from the reference configuration \( r_0 \). Actually, this is true only if \( r^2 \) is not too large. Otherwise, many ‘thermodynamically identical’ configurations, differing only by a permutation of the particles or a discrete translation of step \( L \), will be contained in the hypersphere \((1/N)|r - r_0|^2 = r^2\), and some ‘Gibbs correction factor’ will be needed in the configurational integral in equation (6). The effective potential \( v(r^2) \) and the free energy \( f(\epsilon) \) are related by the Legendre transform

\[
v(r^2) = \max \left[ f(\epsilon) + \frac{3T}{2} \ln(\epsilon/\epsilon_0) - \epsilon r^2 \right].
\]  

Note that \( f(\epsilon) + (3T/2) \ln(\epsilon/\epsilon_0) \) is a convex function. Since \( \lim_{\epsilon \to 0} f(\epsilon) = f_{eq}(T) \), and\(^2\) \( \lim_{\epsilon \to 0}(\partial f/\partial \epsilon)(\epsilon) = 0 \), from equation (9) one then finds

\[
\lim_{r^2 \to \infty} \left[ v(r^2) + \frac{3T}{2} \ln(r^2/r_{max}^2) \right] = f_{eq}(T),
\]

where \( r_{max}^2 = 3/(2e^{1/3} \rho^{2/3}) \). This equation has a simple interpretation: when \( r^2 \) is large, the hypersphere \((1/N)|r_0 - r|^2 = r^2\) contains every configuration of the liquid (modulo a permutation or a translation of step \( L \)) a number of times given by the ratio between the volume of the hypersphere and the volume \( V^N/N! \) of the ‘physical’ phase space, that is \((r^2/r_{max}^2)^3N/2\). This is the ‘Gibbs correction factor’, by which the configurational integral in equation (6) should be divided, when \( r^2 > r_{max}^2 \), to obtain the equilibrium free energy. Therefore, the effective potential \( v(r^2) \) represents the constrained free energy only when \( r^2 < r_{max}^2 \). On the other hand, when \( r^2 > r_{max}^2 \), the liquid is essentially not constrained, and its free energy is \( f_{eq}(T) \). Putting together equations (8) and (10), the equilibrium free energy can be computed, obtaining

\[
f_{eq}(T) = u_{eq}(T) + T \left[ \ln(\rho \lambda^3/\epsilon) + \frac{3}{2} \int_0^\infty \vartheta(r^2) \, d\ln r^2 \right].
\]  

In a ‘mean field’ picture, it may happen that the effective potential \( v(r^2) \) has a metastable minimum at some ‘Edwards-Anderson’ msd \( r_{EA}^2 \). As was mentioned before, in a finite dimensional system with short range interactions, the free energy barriers remains finite when the number of particles goes to infinity, due to nucleation effects. Phase coexistence then implies that \( v(r^2) \) is a convex function\(^3\). Nevertheless, at temperatures near or below the mode-coupling temperature \( T_c \), if we let the system evolve from the configuration \( r_0 \), it will remain trapped for a very long time at some msd \( r_{EA}^2 \) from \( r_0 \), that corresponds to the plateau in \( \langle r^2(t) \rangle \) observed in the free evolution. If the time needed to escape from the metastable state is longer than the time needed to thermalize inside it, one can effectively define the free energy of the metastable state as the constrained free energy \( v(r_{EA}^2) \). The complexity, defined as \( \Sigma = (1/N) \ln N \), where \( N \) is the number of metastable states, can then be computed as the difference between the constrained

\(^2\) This can be derived noting that \( (\partial f/\partial \epsilon)(\epsilon) \) is the thermal average of \( (\partial H_{eq}/\partial \epsilon)(r_0, r) \), that goes to zero when \( \epsilon \to 0 \).

\(^3\) Note however that \( v(r^2) \) has not to be convex when \( r^2 > r_{max}^2 \), because in that region it does not represent the constrained free energy.

doi:10.1088/1742-5468/2005/02/L02001
Effective potential in glass forming liquids

Figure 1. Open circles: function $\vartheta(r^2)$ in LJBM for temperature $T = 0.5$. The Edwards–Anderson msd is chosen (somewhat arbitrarily) to be $r_{EA}^2 = 0.04$, that corresponds to the maximum of $\vartheta(r^2)$, and is also close to the plateau in $\langle r^2(t) \rangle$ observed in the free evolution. The interval in which points are well fitted by the dashed curve is characterized by phase coexistence. The critical coupling, corresponding to the first-order transition, is $\epsilon_c = 1.05 \pm 0.10$ for this temperature.

free energy $v(r_{EA}^2)$, and the equilibrium one $f_{eq}(T)$, divided by the temperature. We are supposing here that the ‘constrained potential energy’ $\langle U(r)/N \rangle_{r_{EA}^2}$ coincides with the equilibrium one $u_{eq}(T)$, which is in principle assured only if $r_{EA}^2$ is a real minimum of $v(r^2)$, so that metastable states have infinite lifetime.

When the temperature is low enough, a first-order transition line in the $\epsilon-T$ plane is expected to appear. When this happens, there will be an interval in $r^2$, corresponding to the coexistence of two different phases in the system, where the effective potential will be a linear function of $r^2$, namely $v(r^2) = v_0 - \epsilon_c r^2$, where $\epsilon_c$ is the critical value of $\epsilon$ for that temperature. In terms of $\vartheta(r^2)$, in the coexistence interval it will be $\vartheta(r^2) = 1 - (2\epsilon_c/3T)r^2$.

This formalism can be applied to a hard sphere liquid as well. In that case, evaluating $\langle (r - r_0) \cdot \nabla U \rangle_{r^2}$ as a temporal average, and since the time integral of the force $-\nabla U$ is equal to the momentum variation $\Delta p$, the function $\vartheta(r^2)$ can be computed as

$$\vartheta(r^2) = \lim_{\Delta t \to \infty} \frac{\beta}{3N\Delta t} \sum_i (r_0 - r_i) \cdot \Delta p_i \bigg|_{r^2}$$

(12)

where the sum is over all the collisions having place in the interval of time $\Delta t$, $r_i$ and $\Delta p_i$ are the coordinates and momentum variations at the time of the $i$th collision, and the liquid is constrained to move at fixed msd $r^2$ from the configuration $r_0$.

I have computed the function $\vartheta(r^2)$ in a well known binary mixture of particles interacting by a Lennard-Jones potential (LJBM) [10], namely a mixture of 80% A particles and 20% B particles, with pair potential $v_{\alpha\beta}(r) = 4\epsilon_{\alpha\beta}[(\sigma_{\alpha\beta}/r)^{12} - (\sigma_{\alpha\beta}/r)^6]$, where $\epsilon_{AA} = 1$, $\sigma_{AA} = 1$, $\epsilon_{AB} = 1.5$, $\sigma_{AB} = 0.8$, $\epsilon_{BB} = 0.5$, and $\sigma_{BB} = 0.88$. I simulate the
Effective potential in glass forming liquids

Figure 2. Solid curve: effective potential \( v(r^2) \) in LJBM for temperature \( T = 0.5 \). The potential is computed by equation (8), integrating a function that interpolates the measured values of \( \vartheta(r^2) \), and setting \( \hbar = m = 1 \). The dotted line corresponds to \( f_{eq}(T) \), computed by equation (11) corrected for mixtures (see the text). As in figure 1, the interval fitted by the dashed curve is characterized by phase coexistence. The difference \( [v(r^2_{EA}) - f_{eq}(T)]/T \) gives the complexity, that is \( \Sigma = 0.55 \pm 0.03 \) for this temperature.

In the case of mixtures, in previous equations one has to substitute \( N! \) with \( N_A!N_B! \). Moreover, \( \epsilon_0 \) has to be multiplied by the factor \((x_A^{x_A} x_B^{x_B})^{2/3}\), where \( x_A \) and \( x_B \) are the fractions of A and B particles, and \( r^{2}_{max} \) has to be divided by it. Therefore, for this system one has \( r^{2}_{max} = 0.4220 \). Finally, the free energy in equation (11) gets an extra contribution \( T(x_A \ln x_A + x_B \ln x_B) \).

The number of particles simulated is \( N = 1000 \), in a box of side \( L = 9.4 \), with pair potential truncated at a distance \( 2.5\sigma_{\alpha\beta} \) and shifted. First of all, a configuration \( r_0 \) is thermalized at temperature \( T \), and kept fixed. Then, the system is cloned, copying configuration \( r_0 \) into new variables \( r \). Subsequently, configuration \( r \) is allowed to evolve, until the msd \((1/N)|r - r_0|^2\) is equal to \( r^2 \). At this point, while \( r_0 \) is still kept fixed, \( r \) is simulated by constraining the msd to remain constant, by means of the RATTLE algorithm [11]. It is then necessary to ‘thermalize’ configuration \( r \), by letting it evolve onto the hypersphere for a sufficient time. Finally, a time average of \( \beta[(r - r_0) \cdot \nabla U]/3N \) is computed to evaluate \( \vartheta(r^2) \). This procedure can be repeated many times, with different and independent configurations \( r_0 \), to average ‘over the disorder’, and evaluate the errors as standard deviations.

In figure 1, the function \( \vartheta(r^2) \) for temperature \( T = 0.5 \) is plotted. It shows a maximum at \( r^2 = 0.04 \), that is very close to the plateau observed in \( \langle r^2(t) \rangle \), when the system is allowed to evolve freely. This can be then identified with the Edwards–Anderson msd \( r^2_{EA} \). The interval where \( \vartheta(r^2) \) is well fitted by the function \((2\epsilon_c/3T)r^2\) corresponds to the coexistence of two phases in the system. The measured values of \( \vartheta(r^2) \) were interpolated
Effective potential in glass forming liquids

by a smooth function, that was then integrated to obtain the effective potential $v(r^2)$ by equation (8), which is plotted in figure 2. Here, the interval of phase coexistence is signalled by the fit with the function $v_0 - \epsilon_c r^2$. Note that the msd $r^2_{\text{max}}$ marks the crossover between the constrained liquid for $r^2 < r^2_{\text{max}}$, whose free energy is $v(r^2)$, and the ‘unconstrained’ liquid for $r^2 > r^2_{\text{max}}$, whose free energy is $f_{\text{eq}}(T)$. The complexity for this temperature is equal to $\Sigma = 0.55 \pm 0.03$, a value compatible with the one measured in the inherent structure formalism within the ‘harmonic approximation’ [12].

I have repeated the simulations for a lower temperature $T = 0.45$. Figure 3 shows the difference between the effective potential $v(r^2)$ and the equilibrium free energy $f_{\text{eq}}(T)$ for the two temperatures. It can be seen that, by lowering the temperature, the effective potential gets more flat in the coexistence region $r^2_{\text{EA}} < r^2 < r^2_{\text{max}}$, and therefore the critical coupling $\epsilon_c$ decreases, as shown in the inset. Extrapolating the $T-\epsilon$ curve, one sees that the Kauzmann temperature should lie around $T_K \simeq 0.35$, a value compatible with the one measured in [12] or [8].

When the system is homogeneous, the distribution of the square displacements of the particles is expected to be Gaussian, $P(r^2) \propto r^2 \exp(-3r^2/2\langle r^2 \rangle)$ (here we denote by $r^2$ the square displacement of a single particle, and by $\langle r^2 \rangle$ the msd). On the other hand, when two phases coexist in the system, we expect that the distribution is given by the superposition of two Gaussians, plus a contribution from the interface. This is shown in figure 4, where the distribution measured in the system constrained at msd $\langle r^2 \rangle = 0.25$ is plotted. On the average, a fraction 0.61 of the particles belongs to the ‘bound phase’, with msd 0.053, and a fraction 0.23 to the ‘unbound phase’, with msd 0.73. The remaining fraction of particles makes up the interface between the two phases. This ‘non-Gaussian heterogeneity’ shows up also in the free evolution of the system [13].

In conclusion, I have applied the effective potential formalism to glass forming liquids, revealing the presence of a first-order transition in the $\epsilon-T$ plane, between two phases

Figure 3. Difference between the effective potential $v(r^2)$ and equilibrium free energy $f_{\text{eq}}(T)$ in LJBM for temperatures (from top to bottom) $T = 0.5$ and 0.45. Inset: critical value of the coupling $\epsilon_c$ as a function of the temperature. The dashed curve is only a guide for the eye.
Effective potential in glass forming liquids

Figure 4. Open circles: distribution of the square displacements of the particles, when the msd is constrained to be \( \langle r^2 \rangle = 0.25 \). Solid curves: two Gaussian distributions, with msd 0.053 and 0.73, and weights 0.61 and 0.23.

characterized by low and high mean square displacement with respect to a quenched reference configuration. It would be interesting to understand how much of this picture is relevant to the dynamical behaviour of the system. Indeed, near or below the mode-coupling temperature \( T_c \), the relaxation times may be connected to the free energy barrier that must be overcome to nucleate an ‘unbound bubble’ inside the sea of bound particles.

It is a pleasure to thank A Coniglio for many fruitful discussions. This work was partially supported by INFM-PRA (HOP), MURST-PRIN-2003, and MIUR-FIRB-2002.

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doi:10.1088/1742-5468/2005/02/L02001